

GLYPHOSATE (M4):1.2 Production and use
DRAFT

1.2 Production and use

1.2.1. Production Process

(a) *Manufacturing processes*

Glyphosate was first synthesized in 1950 as a possible pharmaceutical compound by Cilag (Switzerland), but its herbicidal activity was not discovered until re-synthesized and tested by Monsanto Co. (St. Louis, MO) in 1970 (Székács and Darvas, 2012). The isopropylamine, sodium and ammonium salts were introduced by Monsanto Co. in 1974, and the trimesium (trimethylsulfonium) salt introduced in Spain (1989) by ICI Agrochemicals (now Zeneca Agrochemicals). The original patent protection expired outside the U.S. in 1991 and in the U.S. in 2000, expanding production to other major agrochemical manufacturers [e.g., Dow (U.S), Syngenta (Switzerland), NuFarm (Australia), as well as large-scale production in China (e.g., Shenzhen Jiangshan), but the leading preparation producer remained Monsanto (Duke & Powles, 2008).

Glyphosate is a phosphonomethyl derivative of the amino acid glycine (with one of the amino hydrogen atoms of glycine replaced by a phosphonomethyl group) and its name is derived from the words glycine and phosphonate (Jayasumana, et al., 2014). While an organophosphorus compound, glyphosate does not contain the organophosphate ester associated with cholinesterase inhibition. There are two dominant families of commercial production of glyphosate, the “alkyl ester” pathways and the “iminodiacetic acid (IDA)” pathways, with IDA produced from iminodiacetonitrile (IDAN, produced from hydrogen cyanide, or HCN), diethanol amine (DEA), or chloroacetic acid (Dill et al., 2010; Tian et al., 2012). In the “one pot” alkyl ester process (dominant among Chinese manufacturers), glycine is added to a mixture of triethylamine and paraformaldehyde in methanol, producing a hydroxymethylglycine intermediate. Subsequently, DMP is added to form phosphonate ester; concentrated HCl is added to remove the hydroxymethyl group; and heating produces further hydrolysis of the phosphonate ester to glyphosate. For the IDA route (dominant outside of China, e.g., by Monsanto), the hydrochloride salt of IDA undergoes phosphonomethylation via a modified Mannich reaction to form N-phosphonomethyliminodiacetic acid (PMIDA); after isolating PMIDA, the protecting group is removed via oxidation to form glyphosate (Dill et al., 2010).

To further increase water solubility of technical grade glyphosate acid, it is formulated as its isopropylamine, monoammonium, potassium, sodium or trimesium salts. Most common is the isopropylamine salt, which is formulated as a liquid concentrate (5.0-62% ai), ready-to-use liquid (0.5 to 19.7% ai), pressurized liquid (0.75-0.96% ai), solid (75-94% ai), or

pellet/tablet (60-83% ai) (EPA, 1993). There are reportedly over 750 products containing glyphosate for sale in the U.S. alone (NPIC, 2010). Formulated products contain various non-ionic surfactants, most notably polyethyloxylated tallowamine (POEA), to facilitate uptake by plants (Székács and Darvas, 2012). Formulations might contain other active ingredients such as simasine, 2,4-D, or MCPA (IPCS, 1996), with herbicide resistance driving demand for new formulations with multiple active ingredients (Freedonia, 2012).

(b) Production volume

Glyphosate is believed to be manufactured by at least 91 producers in 20 countries, including 53 in China, nine in India, five in the U.S., four in Singapore, three in Singapore, Taiwan, and Mexico, two in Spain, and one each in Australia, Canada, Cyprus, Egypt, Germany, Guatemala, Hungary, Israel, Malaysia, Thailand, Turkey, the U.K., and Venezuela (Farm Chemical International, 2015). Production and use of glyphosate have risen dramatically due to the expiration of patent protection in 1991 (except U.S.) and 2000 (U.S.), with increased promotion of non-tillage agriculture, and with the introduction in 1996 of genetically modified glyphosate-tolerant crops (Székács and Darvas, 2012). In the U.S. alone, over 80 million kg (estimated) of glyphosate were used in 2007 (rising from less than 4 million kg in 1987) (EPA, 2011; EPA, 1997). This rapid growth rate was also observed in India, where production increased from 0.31 million kg in 2003/2004 to 2.1 million kg in 2007/2008 (MCF, 2008) and glyphosate use increased nearly 50% from 2.1 million kg in 2007 to 3.1 million kg in 2008 (Monsanto India, 2008). Glyphosate now is believed to be the most heavily used herbicide in the world (CRI, 2013), with an annual global production volume estimated as approximately 600 million kg in 2008 (Dill et al., 2010) and rising to about 650 million kg in 2011 (CCM, 2011), and to 720 million kg in 2012 (Transparency Market Research, 2014). China currently produces more than 40% of the global glyphosate supply and exports almost 35% of the world supply (Hilton, 2012) and has sufficient production capacity to satisfy total world demand (Yin, 2011). Increased farming of biofuel crops, practice of no-tillage agriculture, and use of genetically modified seeds in the U.S., Brazil, Argentina, South Africa, India, and China is likely to lead to a continued increase in production of glyphosate (Freedonia, 2012; Transparency Market Research, 2014).

1.2.2. Uses

Glyphosate is a broad-spectrum, post-emergent, nonselective, systemic herbicide, effective at killing or suppressing all plant types including grasses, perennials, and woody plants. When applied at lower rates, glyphosate is a plant growth regulator. It has agricultural and non-agricultural uses throughout the world. Glyphosate resistance has become an increasingly severe problem, particularly for producers of corn, cotton, and soybeans (EPA, 1993; Duke and Powles, 2009; Smith, 2014).

(a) Agriculture/Crop Protection

Glyphosate is effective against over 100 annual broadleaf weed and grass species, and over 60 perennial weed species (Dill et al., 2010). Application rates are about 1.5-2 kg/ha for pre-harvest, post-planting, and pre-emergence use; about 4.3 kg/ha as a directed spray in vines; about 4.3 kg/ha in orchards, pastures, forestry, and industrial weed control; and about 2 kg/ha as an aquatic herbicide (Tomlin, 2000). More common application methods include broadcast, aerial, spot, and directed spray applications, while specialized methods include controlled droplet, injection, and frill application, the use of recirculating sprayers, and wiper/wick type applicators (EPA, 1993).

Due to its broad spectrum activity against crops, the use of glyphosate in agriculture were limited until greater adoption of no-till and conservation till practices. Such practices, which require chemical weed control before planting, increase water permeation, organic matter retention, and nutrient cycling in soil, while reducing soil erosion and labor and fuel costs (Dill et al. 2010). The use of both conservation tillage and glyphosate herbicides have grown dramatically with the introduction of several crops (soybeans, corn, cotton, canola, and sugar beet) bioengineered to be glyphosate tolerant (Ware and Whitacre, 2004). Until 1996, use of glyphosate in agriculture was restricted to “post-harvest treatments” when weeds are shooting but crop seeds have not begun to germinate, or for weed control between established rows of tree, nut, and vine crops. The introduction of glyphosate tolerant crops in much of the world has transformed glyphosate to an incrop, post-emergent, selective herbicide for use in annual, agronomic crops (Duke and Powles, 2009). Genetically modified crops accounted for 45.2% of the total glyphosate demand in 2012 (Transparency Market Research. 2014. In Europe, however, “post-harvest treatments” are still the most commonly used management practice.

(b) Residential

Glyphosate widely available for household weed control throughout the world. In the U.S. glyphosate consistently has been the second most commonly used pesticide (behind 2,4-D) in the home and garden market sector for the period between 2001 and 2007, with an annual use of 2-4 million kg (EPA, 2011).

(c) Natural Areas/Rights-of-Ways

Glyphosate was initially utilized to control perennial weeds on ditch banks, in right of ways, and fallow fields (Dill et al., 2010). Glyphosate is effective against grasses, forbs, vines, shrubs, and trees. In the U.S., it is commonly used in invasive management against natural area weeds such as bush honeysuckle, cogon grass, and common buckhorn and has successfully controlled common reed, purple loosestrife, and reed canarygrass in aquatic or wetland systems (Tu et al., 2001). Approximately 1-2 percent of total glyphosate use in the

U.S. is in forest management (Mance, 2012).

(d) Drug Eradication

Glyphosate has played a conspicuous role in the “drug war,” including a massive aerial herbicide-spraying program begun in June of 2000 to reduce cocaine production in Colombia (“Plan Colombia”) (Lubick, 2009) and as a defoliant of marijuana fields in Mexico and South America (Székács and Darvas, 2012)

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